Indian J. Phys. **44**, 339-345, (1970)

Electronic spectra of 2,4-xylenol in different states

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(*Received* 26 *June* 1970—*Revised* 11 *August* 1970)

The ultraviolet absorption spectrum of 2, 4-xylenol in vapour state has been recorded and analysed. The spectrum is found to consist of weak absorption bands with the 0,0 band at 35312 cm^{-1}. The vibrational analysis indicates that the band system of the molecule is due to an allowed transition and the weakness of absorption has been attributed to small migration moment. The spectra of the substance in the liquid and solid states and in a solution of cyclohexane have also been recorded and the observed results discussed.

Introduction

The dependence of intensity of bands in the near ultraviolet absorption spectra of polysubstituted benzene compounds on the resultant migration moment was discussed by Sklar (1942). Sponer (1947) reported analysis of absorption spectra of several trichloro- and trimethyl benzenes in vapour state and observed that the intensity of absorption is large for molecules like 1, 2, 4-$C_6H_3X_3$ molecules, while for molecules like 1, 2, 3-$C_6H_3X_3$ the intensity is very small and the 0, 0 band is absent though the transition is allowed by symmetry. The results are in accord with the idea of Sklar that for 1, 2, 4-$C_6H_3X_3$ molecule the migration moment vectors add to give a large resultant moment, whereas, for molecules like 1, 2, 3-$C_6H_3X_3$ this resultant is zero. Sklar's idea was later extended by Platt (1951) to different substituents in benzene and other large ring molecules.

Analyses of absorption spectra of only a few trisubstituted benzene compounds with different substituents (with different X) have been reported in literature. A programme was undertaken to record and analyse the spectra of a few such compounds in vapour state. The results obtained with 2,4-xylenol and its spectra in liquid and solid states and in solution were recorded, and the observed results are reported in this paper.

Experimental

The chemically pure sample of 2, 4-xylenol was obtained from B.D.H. The sample was carefully fractionated and proper fraction was distilled under reduced pressure before use.

To study the absoption spectra of 2, 4-xylenol in the vapour phase at different temperatures, absorption cells usually long tubes of different lengths provided

with quartz windows were used. The liquid was kept in a bulb connected to the absorption cell by a side tube. The bulb was placed inside a box heater and the absorption tube was placed inside a cylindrical heater, the temperature of which was kept about 10°C higher than that of the box heater. The absorption tubes together with the attached bulbs were evacuated and sealed off. The best spectogram was obtained with a 100 cm vapour tube maintained at 37°C. Increase in temperature of the tube did not result in any improvement of intensity of the bands. To identify the 0, 0 band and eliminate bands due to $v—v'$ transition, a 30 cm vapour tube was taken and the temperature of the bulb was varied to obtain different pressures of the absorbing vapour.

The experimental arrangements for studying photographically the absorption spectra of 2, 4-xylenol in the liquid state at room temperature, in the solid state at —180°C and in solution in specpure cyclohexane at 32°C were the same as those used by earlier workers, *viz.* Banerjee (1956), Sirkar & Misra (1959).

The absorption spectra were photographed on Kodak Spectrum Analysis No. 1 film with an Adam Hilger all metal E1 spectrograph (E 478) having dispersion of about 2 5Å/mm in the 2600Å region. Iron arc spectrum was also photographed with a Hartmann diaphragm on each film for comparison.

Microphotometric records of the spectra were taken with a Kipp & Zonen type self-recording Moll microphotometer. The method of determination of the positions of the absorption maxima was the same as that given by Banerjee (1956). The accuracy in the measurements of positions of the absorption peaks was ± 10 cm^{-1} for narrow bands and ± 20 cm^{-1} for broader bands while the uncertainty in the case of broad diffuse bands was much larger.

The Raman spectrum and the state of polarization of Raman lines were photographed in a Fuess glass spectrograph, and the infrared absorption bands of the sample were recorded in the usual way with a Perkin Elmer Model 21 spectrophoto meter fitted with rock salt optics (Chattopadhyay & Mukerjee 1967).

Results

The microphotometric records of the absorption spectra of 2, 4-xylenol in the vapour, liquid and solid states and in solution in cyclohexane are reproduced in figures 1 and 2. The positions of the absorption maxima, their relative intensities and probable assignments are given in tables 1, 2 and 3.

The vibrational spectra of 2, 4-xylenol were only partially reported by earlier authors. The infrared spectra and the Raman spectra with state of polarization of the lines of this compound were also recorded. These data are included in table 4.

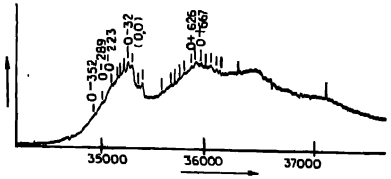

FIGURE 1. Microphotometric records of the ultraviolet absorption spectra of 2, 4-xylenol in the vapour state at 37°C.

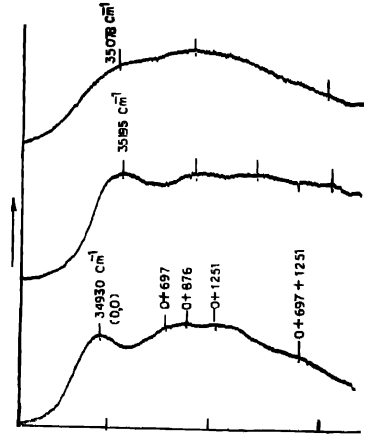

FIGURE 2. Microphotometric records of the ultraviolet absorption spectra of 2, 4-xylenol in different states and in solution.
a) Liquid state at 26°C
b) Solid state at −180°C
c) 8.5×10^{-4}M solution of 2, 4-xylenol in cyclohexane at 32°C

DISCUSSION

The spectrum in the vapour state

The molecule of 2, 4-xylenol may at most be assumed to belong to C_s point group, and the electronic transition corresponding to $A_{1g} - B_{2u}$ transition in benzene would be an $A' - A'$ transition which is allowed by symmetry of the molecule. The absorption spectrum due to the vapour consists of four groups of bands. Each group consists of several narrow bands degraded towards the red. The

band at 35312 cm^{-1} in the first group is found to persist with relatively undiminished intensity at lower pressures of the absorbing vapour and has been taken as the 0, 0 band of the system. The bands on the larger wave length side could then be assigned to $v-o$ and $v-v$ transitions as indicated in table 1.

TABLE 1. Ultraviolet absorption spectrum of 2, 4-xylenol in the vapour state at 37°C

Wave No. in cm^{-1} of absorption band with intensity	Difference from the 0, 0 band	Assignment
34960 vw	— 352	0—352
35023 w	— 289	0—289
35089 m	— 223	0—223
35310 m	— 158	0—158
35180 m	— 132	0—132
35235 ms	— 77	0— 77
		0—289+212
35280 s	— 32	0— 32
		0— 132+100
35312 s	0	0, 0
35382 vw	70	0+ 70
35412 ms	100	0+100
35437 vw	125	0+125
35524 vw	212	0+212
35582 w	270	0+270
35633 m	321	0+321
35780 w	468	0+468
35832 m	520	0+520
35903 m	591	0+626—32
35938 s	626	0+626
35979 s	667	0+667
36028 w	716	0+626+100
36080 w	768	0+667+100
36134 m	812	0+812
36186 m	874	0+874
36359 ms	1049	0+2×520
36538 m	1226	0+1226
36572 m	1260	0+2×626
36602 w	1290	0+626+676
36804 vw	1492	0+626+874
37202 vvw	1870	0+3×626

TABLE 2. Ultraviolet absorption spectra of 2, 4-xylenol in the liquid and solid states

Liquid at 26°C		Solid at −180°C	
Wave no. in cm^{-1} with intensity	Separation between the successive bands in cm^{-1}	Wave no in cm^{-1} with intensity	Separation between the successive bands in cm^{-1}
35078 (ms)	779	35195 (s)	746
35857 (s)	1169	35941 (ms)	578
37026 (vs)		36519 (m)	728
		37247 (m)	

TABLE 3. Ultraviolet absorption spectrum of 8.5×10^{-4}M solution of 2, 4-xylenol in cyclohexane at 32°C

Wave no. in cm^{-1} with intensity	Assignment
34930 (s)	0,0
35627 (s)	0+697
35806 (ms)	0+876
36181 (m)	0+1251
36882 (m)	0+697+1251

It can be seen that the ground state vibrational frequencies 158, 223, 289 and 352 cm^{-1} observed in the present work agree reasonably with the Raman shifts 153, 212, 281 and 345 cm^{-1}, respectively. The strong band at 35182 cm^{-1} on the long wave length side of the 0, 0 band, which could not be assigned to a $v-v$ transition, most probably represents a $v-0$ transition involving a fundamental vibrational frequency 132 cm^{-1} in the lower state though such a frequency could not be detected in the Raman spectrum. On the short wave length side of the 0, 0 band there is a moderately strong band at 35412 cm^{-1}, which may represent a fundamental excited state vibrational frequency 100 cm^{-1}, corresponding to the ground state vibrational frequency 132 cm^{-1} mentioned above. The correctness of the assignments is probably supported by the fact that there is also a band at 35280 cm^{-1} on the long wave length side of the 0, 0 band and separated by 32 cm^{-1} from it which may be readily assigned to a $v-v$ transition involving the two vibrational frequencies 132 cm^{-1} and 100 cm^{-1} in the upper and the lower states, respectively. The excited state frequency 70 cm^{-1} may represent a suitable torsional mode in the molecule.

TABLE 4. Raman and infrared frequencies of 2, 4-Xylenol at 28°C

Raman shift in cm^{-1} (Magat, 1936)	Raman shift in cm^{-1} (present work)	Infrared frequency in cm^{-1} with intensity (present work)
	153 (1) D	
212 (5)	210 (4) D	
278 (4)	281 (3) D	
348 (5)	345 (5) D	
446 (4) D	448 (5) D	
490 (5)	489 (6) P	
572 (6)	571 (6) P	
717 (8)	721 (10) P	710 (m)
770 (7)	770 (8) P	760 (s)
	810 (0)	804 (vs)
	874 (0)	868 (m)
930 (5)	932 (6) P	924 (m)
1032 (0)	1035 (0)	1005 (m)
		1030 (m)
	1122 (1)	1112 (vs)
	1150 (2) P	1145 (s)
	1190 (1)	1194 (vsb)
1265 (6)	1265 (8) P	1260 (vs)
	1324 (0)	1330 (sb)
1379 (6)	1383 (7) P	1376 (s)
	1417 (1) D	1410 (s)
1449 (1)	1459 (1) D	1452 (s)
	1510 (0)	1505 (vs)
1610 (5)	1600 (2)	1605 (m)
	1614 (8b) D	
2732 (1)	2740 (2) D	
2862 (5)	2875 (4) P	
2917 (10)	2920 (10) P	2925 (s)
3034 (5)	3055 (6) P	3035 (m)
3203 (2)		

As can be seen from tables 1 and 4 that the excited state frequencies observed in the present investigation may be correlated with the observed Raman and infrared frequencies with a fair degree of agreement. The prominent excited state frequencies 520, 626, 667 and 874 cm^{-1} occur also in combinations. They may be correlated with the ground state frequencies 571, 721, 770 and 932 cm^{-1}, respectively, all of which arise from symmetric modes belonging to a'-species, as is

indicated by the fact that the corresponding Raman lines are polarised. The general vibrational structure of the absorption spectrum of the molecule thus conforms to an electronic transition allowed by the symmetry of the molecule.

The spectra in liquid and solid states and in solution

In the liquid state 2, 4-xylenol yields very broad bands without any vibrational structure and only the wave numbers of centres of the bands could be measured very approximately. It may be recalled that in the liquid state, molecules of this compound are associated with each other through intermolecular hydrogen bonding (Banerjee & Mukherjee 1966). This may explain the very large width of bands in the spectrum of the liquid. When the liquid is frozen and cooled to −180°C, the bands remain broad and structureless.

The bands in the spectrum due to solution of 2, 4-xylenol in cyclohexane are a little sharper. The bands are somewhat better resolved from each other and the excited state frequencies 697, 876 and 1251 cm^{-1} (corresponding values observed in vapour spectrum are 667, 874 and 1226 cm^{-1}, respectively) could be identified.

ACKNOWLEDGEMENT

The author expresses his grateful thanks to Dr. S. B. Banerjee for continued guidance throughout the progress of the work, and to Prof. G. S. Kastha, D.Sc., for kind interest. He is also indebted to Sri S. C Bag for help in the experimental work and to Sri S Chattopadhyay in recording Raman and infrared spectra.

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